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<p>This report describes the progress in the synthesis, characterization and spectroscopy of soluble polysilanes and germanes. It includes polymer structural studies, theoretical investigations of electronic structure and mechanistic studies of the photodecomposition. It also describes the potential of these materials as polymeric photoconductors, and as new materials for microlithography. The initial work on the nonlinear optical characteristics of these materials is also included.</p> <p style="text-align: right;">K. J. Miller</p>			
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**SOLUBLE POLYSILANES: A NEW CLASS OF RADIATION SENSITIVE  
O<sub>2</sub> - RIE RESISTANT POLYMERS FOR USE IN MICROLITHOGRAPHY**

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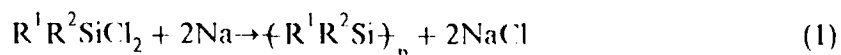
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## INTRODUCTION

Historically, substituted silane polymers are quite old and the first aryl substituted materials were probably prepared in the 1920's. The early materials, however, attracted little scientific attention since they were highly crystalline, insoluble and intractable. The preparation of the first soluble homo and copolymers about 10 years ago initiated the modern era in the study of polysilane chemistry which continues today.<sup>1</sup> The synthesis of a large number of soluble polymers in recent times confirms that the undesirable polymer properties observed for the early derivatives were exceptional and are not generic to the class. It is ironic that in spite of considerable efforts, the original Wurtz-type coupling of substituted dichlorosilanes (Eq. 1) is still the most viable general procedure for the preparation of high molecular weight, linear polysilane derivatives. Over the course of this contract, we have studied the heterogeneous polymerization of dichlorosilanes to polysilanes in great detail. A number of representative monomer classes were selected for study and the effects of metal reagent type, particle size, reaction temperature, solvent, the presence or absence of complexing additives etc. were exhaustively examined.<sup>2</sup> Although no single set of reaction conditions was found to be applicable for every monomer class, the data accumulated allows us to predict, based on the nature and reactivity of the monomer, a set of conditions likely to lead to successful polymerization. This data base has greatly facilitated the synthesis of interesting new materials. These techniques have proved useful not only for the preparation of polysilane homo and copolymers, but also for the generation of block interrupt polysilanes (polysilane blocks decoupled by heteroatom substitution) and high molecular weight soluble polygermanes.



## SPECTRAL AND ELECTRONIC PROPERTIES

It was the curious electronic properties of catenated silane oligomers which first attracted the attention of both theorists and experimentalists.<sup>3</sup> The spectral properties were consistent with significant delocalization of the sigma electrons in the polymer backbone. All soluble, high molecular weight polysilane derivatives absorb strongly in the UV. Solution UV spectroscopic studies show that alkyl substituted polysilanes absorb in the region 300-325 nm, and the position of the absorption maximum depends on the steric bulk of the substituents.<sup>4</sup> Aryl substituents directly bonded to the backbone cause a red shift of 20-30 nm due to the electronic interaction of the substituent  $\pi$  orbitals with those of the silicon backbone. The absorption characteristics of linear substituted silane polymers also depend on the extent of catenation.<sup>4</sup> In this regard, both the positions of the long wavelength absorption maxima and the molar absorptivities per silicon-silicon bond increase rapidly at first with increasing molecular weight, but approach limiting values beyond a degree of polymerization (chain length) of 40-50 as shown in Figure 1. The gross spectral characteristics of linear silicon catenates have been adequately rationalized computationally by simple linear combination of atomic orbitals (LCAO) or Sandorfy-type theoretical treatments.<sup>3</sup> However, the absorption spectra of the polysilanes also depend strongly on the backbone conformation,<sup>1</sup> a fact which was not predicted from the simple molecular orbital treatments. More sophisticated semiempirical and ab initio studies were required to adequately describe the electronic ground state and the nature of the electronic transitions. INDO/S calculations rationalize the conformational dependence of the absorption spectra in terms of long range 1,4-orbital interactions and predict furthermore that *trans* sequences should absorb at longer wavelengths than *gauche*.<sup>5</sup> Moreover, these studies also suggest that the electronic excitation energy tends to localize in the *trans* segments even when they are quite short. A solution model for the dialkyl polysilanes, which has emerged from

wavelength dependent fluorescence polarization studies, is one of a polymer chain composed of discrete chromophoric segments (presumably *trans* or nearly *trans* units of varying lengths). The individual spectral characteristics depend on the segment length and the chromophores are partially electronically decoupled by conformational twists or kinks. These segments apparently communicate by rapid energy transfer.<sup>6</sup> Such a model is also supported by the INDO/S calculations. Consistently, the experimental absorption and emission characteristics of polysilanes in solution may be adequately modeled<sup>7</sup> using rotational isomeric state theory (RIMS) assuming both a statistical distribution of chromophoric segments of varying lengths, and conformational defects which mediate the electronic interaction between the chromophores. As expected from such a model, the polysilanes are predicted to be thermochromic, as is often the case, although the detailed conformational interpretation of the solution thermochromism<sup>7,8</sup> is complicated by possible aggregation effects.

The understanding of the thermochromic transitions of polysilane derivatives in the solid state has been assisted by structural studies using FT-IR, Raman, NMR and WAXD spectroscopy (*vide infra*). These techniques have been less useful for studying the thermochromism in solution. The studies in solution are exacerbated by the fact that many symmetrically substituted polysilane derivatives precipitate rapidly from solution at low temperatures. We have focussed our studies on two distinct aspects of this problem: (1) what is the structure of the long wavelength absorbing material which is produced at low temperatures and (2) is the actual thermochromic transition consistent with a single molecule event or does aggregation play a role in the thermochromism. Regarding the first question, we have recently prepared noncrystalline, unsymmetrically substituted materials which display the same thermochromic behavior in the solid state as in solution.<sup>9</sup> FT-IR and Raman studies suggest that the backbone structure of the long wavelength absorbing materials is best

described as disordered trans. Future WAXD studies at low temperatures on stretch-oriented film should confirm the proposed structure. The second question has proved far more difficult to answer. Even with the use of more soluble polysilanes, precipitation precludes the use of classical light scattering techniques. Using a dual beam apparatus to simultaneously monitor the temporal behavior of the appearance of the fluorescence of the long wavelength form and the scattering produced by aggregation, we have concluded that both events occur almost simultaneously. However, the enormous increase in the scattering intensities at low temperatures precludes any detailed structural analysis. For this reason, we have turned to small angle neutron scattering (SANS) since this technique is less sensitive to large aggregate particles. Preliminary variable temperature studies using SANS also confirm the rapid formation of aggregates at low temperature. However, analysis of the data at large scattering vectors suggest that even when these aggregates are present, the average persistent length of the polymer in solution is not significantly different from that observed above the thermochromic transition.<sup>10</sup> Analysis of this data is complicated by low intensities at high scattering vectors necessitating long run times. The definitive experiment will require a very bright neutron source such as exists at Grenoble and a collaborative study is underway at this time. Finally, the use of emission spectroscopy allows the study of very dilute solutions ( $10^{-5}$ M or less based on the monomer unit). Detailed variable temperature studies of the excitation-emission spectroscopic behavior of a number of unsymmetrically substituted polysilanes reveals a distinct concentration dependence. This represents the first experimental observation of a concentration dependence for the spectroscopic properties in dilute solutions around the thermochromic transition temperature and suggests the possibility that aggregation is involved in the thermochromic transition even in very dilute solutions. In summary, recent spectroscopic studies on the solution thermochromism suggests aggregation but much work remains to be done in the area.

The fluorescence emission from most polysilane derivatives in solution is short-lived (75-200 ps)<sup>6</sup> and the band width is much narrower than the corresponding absorption bands. The short radiative lifetimes, narrow spectral band widths, and lack of fine structure of the fluorescence is suggestive of a highly delocalized excited state. Comparison of the absorption and emission spectra of poly(di-n-hexylsilane) in solution suggests that emission is occurring from segments containing 20-36 silicon atoms, assuming that the oscillator strength is independent of the chromophore length.<sup>6,11</sup> In contrast to the intense, narrow fluorescence reported for poly(di-n-alkylsilanes), a weak, broad, long-lived emission is often observed at longer wavelengths in rigid media. This has tentatively been attributed to phosphorescence and we<sup>10</sup> and others<sup>7</sup> have suggested that the triplet excitation is more localized and hence may be responsible for the polymer photolability. This suggestion is also consistent with theoretical predictions.<sup>1</sup> While the apparent localized nature of the triplet excitation is more consistent with the observed photolability (*vide infra*), this connection has been unambiguously established by quenching studies only for poly(methyl-n-propylsilane).<sup>12</sup>

Many polysilane derivatives are also strongly thermochromic in the solid state. This effect was first reported for poly(di-n-hexylsilane) (PDHS) (see Fig. 2)<sup>13</sup> and this material has been the object of many structural studies. In this case, crystallization of the n-alkyl side chains enforces an all-trans planar backbone conformation which is responsible for the ~60 nm spectral red-shift. Above the transition temperature, which for PDHS is around 42°C, the backbone conformationally disorders. It appears that for polysilane derivatives with sterically demanding substituents some type of intermolecular interaction in the solid state is necessary to enforce a stable planar all-trans conformation. This characteristic leads to a series of very subtle substituent effects which can dramatically effect the spectral properties. For example,

poly(di-n-pentylsilane) (PDPS), for which side chain crystallization does not occur to a significant extent, adopts a 7/3 helical backbone conformation in the solid state at room temperature.<sup>14</sup> For this polymer, a deviation in the backbone of only  $\sim 30^\circ$  from trans planar results in a spectral blue-shift of almost 60 nm!

Recent studies suggest, however, that side chain crystallization does not always assure the formation of a stable, planar, all-trans backbone conformation for polysilanes with sterically demanding alkyl substituents. For example, poly(di-n-tetradecylsilane) (PDTDS) adopts a non-planar TGTG' backbone conformation in spite of spectral evidence of side chain crystallization.<sup>14</sup> Apparently, the backbone retains sufficient flexibility for derivatives with long chain n-alkyl substituents, even in the presence of strong intermolecular interactions to allow alternative non-planar conformations. It is also interesting that PDTDS is still thermochromic, suggesting that the observation of a spectral red-shift need not necessarily be uniquely associated with the formation of planar all-trans backbone segments. We have also observed that the introduction of sterically unsymmetrical substituents such as aryl groups, which can minimize intrachain steric interactions by rotation around the silicon-carbon substituent bond, can also produce dramatic spectral effects. For example, the poly(bis-alkylphenylsilanes) are the most red-shifted of all of all polysilane derivatives ( $\lambda_{\max} \sim 400\text{nm}$ ) and additional spectral data supports the presence of long trans sequences which persist even in solution.<sup>15</sup>

The delicate conformational balance in the poly(diarylsilanes) is extremely sensitive to substituent effects. For example, poly(bis-p-alkoxyphenylsilane) derivatives absorb at very short wavelengths and are both thermo and solvatochromic. We have proposed that unfavorable substituent dipole interactions in the all trans confirmation cause considerable twisting of the polymer backbone.<sup>16</sup> This represents another



striking example of how very subtle substituent effects can drastically alter the spectral properties of polysilane derivatives.

The strong long wavelength electronic absorption observed for alkyl substituted silane high polymers is a  $\sigma\sigma^*$  transition and is polarized along the polymer backbone. Orientational techniques can therefore introduce a highly anisotropic polarizability and strong linear dichroism. We demonstrated this first by solution flow extension techniques (flow dichroism) and later by polymer stretch alignment.<sup>6</sup> Recently, we have shown that in the solid state certain polysilanes undergo a thermal transition to a columnar liquid crystalline hexagonal array capable of orientation by standard liquid crystal techniques.<sup>17</sup> We have also demonstrated that certain phenylalkyl substituted polysilanes  $[(\text{PhSiR})_n \text{ R} = n - \text{alkyl}]$  are very rigid in solution and form lyotropic liquid crystalline solutions at high polymer concentrations. The polymers chains in these solutions can subsequently be oriented by flow extension, shear alignment, gel spinning, etc.<sup>18</sup>

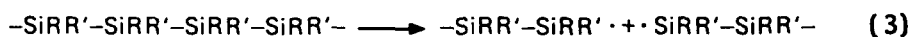
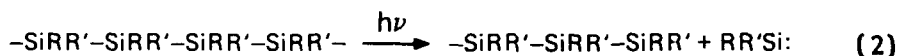
We have also prepared the first ordered Langmuir-Blodgett monolayers from rigid poly(diarylsilanes).<sup>19</sup> The polymer chains in these structures are extended in the dipping direction and the layers are strongly dichroic. The capacity for polymer alignment and its effect on the electronic properties is an important characteristic of polysilane derivatives and is worthy of future studies.

## RADIATION SENSITIVITY

Polysilane derivatives are sensitive to light and ionizing radiation both in solution and in the solid state. Irradiation causes a rapid bleaching of the long wavelength absorption, and the formation of lower molecular weight fragments.<sup>20</sup> The spectral bleaching, which is key to a number of applications (vide infra) is unusual and occurs because the absorption characteristics are a function of polymer molecular weight. We

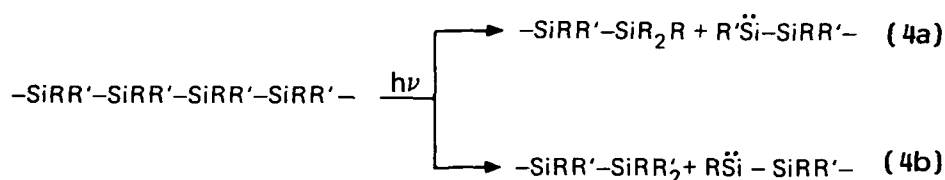
have measured quantum yields for polymer scission in solution as high as (0.25-1.0) although competitive crosslinking is often observed, particularly when pendant unsaturated substituents are directly attached to the polymer backbone<sup>20</sup> The efficiency of both processes decreases markedly (50-100 fold) in the solid state. However, in every case that we have examined, photoscissioning predominates and this behavior can be considered to be characteristic of the linear polysilanes.

Exhaustive irradiation of soluble polysilanes at 254 nm in solution in the presence of trapping reagents such as trialkylsilanes or alcohols suggests that both silylenes and silyl radicals are intermediates (Equations 2 and 3). Thermodynamic considerations and our experimental studies have shown that the silylene-forming reaction and the pathway to the silyl radicals are uncoupled and competing processes. In many respects, the photochemical decomposition of substituted silane high polymers resembles that previously reported for shorter chain oligosilanes.



However, recent mechanistic studies in solution suggest that the polymer photochemistry is more complex than first imagined. There is an unusual wavelength dependency and the quantum yield for the extrusion of silylenes decreases markedly with increasing irradiation wavelength, becoming very small above 300 nm.<sup>21</sup> On the other hand, the photodegradation proceeds at all wavelengths absorbed by the polymer as evidenced by the continuous spectral bleaching and decrease in molecular weight. Studies on isotopically labeled polymers show that silyl radicals produced by polymer chain scission disproportionate in addition to recombining. In addition, we have

identified a new photochemical chain-cleavage reaction, i.e., 1,1-reductive elimination (see Equations 4a and 4b).<sup>22</sup> The wavelength dependent photochemistry has been rationalized in terms of the proposed solution model for the polysilanes consisting of a statistical collection of chain segments of varying lengths with differing absorption characteristics which are only weakly electronically coupled due to conformational defects.<sup>6,12</sup>



In summary, mechanistic studies in solution suggest that there are at least three photochemical pathways leading to polysilane molecular weight reduction: (i) substituted silylene extrusion and chain abridgement; (ii) silicon-silicon bond homolysis to produce chain-cleaved silyl radicals and (iii) 1,1-reductive elimination to produce chain silylenes. Current evidence indicates that these pathways are uncoupled and competing.

## APPLICATIONS

The intense scientific investigation of substituted silane high polymers has resulted in the discovery of several potential applications. They have been utilized as (1) preceramic precursors to silicon carbide (2) broad spectrum, oxygen insensitive photo initiators for vinyl polymerizations (3) a new class of polymeric photo and charge conductors (4) materials for high resolution microlithography and recently (5) materials with interesting nonlinear optical properties. In the course of our investigations, we have studied applications 3-5.

### Photo and Charge Conduction

We have demonstrated that thermally stimulated current spectroscopy (TSC), a technique formerly used primarily for trap spectroscopy, can be utilized to study hopping transport in amorphous polymers such as polysilanes.<sup>23</sup> A unique feature of this technique is the ability to distinguish between transport mechanisms which differ only slightly in activation energy. We have applied this technique to the study of interchain charge transport in polysilanes and find activation parameters in agreement with those measured by more traditional time-of-flight (TOF) techniques. In addition, we have detected and studied the radiation induced production of surface charge traps. The hole mobilities for the polysilanes are the highest measured for any amorphous polymer and this coupled with their excellent discharge capacity suggests possible xerographic applications.<sup>1</sup>

### Microlithography

The polysilanes have a number of unique material characteristics for certain lithographic applications, particularly those utilizing multilayer techniques. They are (i) thermally and oxidatively stable yet photochemically labile; (ii) strongly absorbing over a broad spectral range, yet bleachable; (iii) good film formers which are incompatible with most common organic carbon polymers; (iv) high in silicon content and hence, very resistant to etching under oxygen plasma conditions and (v) sensitive not only to light but also various types of ionizing radiation ( $\gamma$ -ray, X-ray, e-beam, etc.). This combination of characteristics is ideally suited for a variety of multilayer lithographic processes.<sup>20,24</sup> Accordingly they have been used as soluble, oxygen reactive ion etch ( $O_2$  - RIE) resistant barrier layers in trilayer schemes, as new resists for ionizing radiation imaging, as combined imaging and etch barrier layers in bilayer processes utilizing both wet and dry development techniques and as short wavelength contrast enhancing materials. Space limitations prevent the detailed discussion of each

application and the interested reader is referred to the reference list. The important concepts of bilayer imaging and contrast enhancement are discussed in more detail below.

Multilayer resist imaging schemes for the production of high resolution images offer certain advantages, particularly where troublesome chip topography causes difficulties for single layer schemes. In a bilayer process (see Fig. 3) the substrate with its topographic features is initially coated with a thick ( $1\text{-}5\mu\text{m}$ ) layer of a planarizing polymer which is usually not photosensitive. A thin imaging layer ( $0.15\text{-}0.5\mu\text{m}$ ) is then coated on top of the planarizing layer. Upon exposure, the top layer can be imaged and developed with high resolution because the imaging layer is very thin, flat and of uniform thickness. In principle, the initial development could be either by a classical wet process or by dry, photoablative development. Transfer of these high resolution images through the planarizing polymer layer is usually accomplished by  $\text{O}_2$  - RIE plasma techniques, since highly anisotropic etching conditions can be employed to assure that the transfer of the initial photoimages maintains near-vertical side wall profiles. The successful utilization of such a scheme requires a photosensitive imaging layer which is also significantly more resistant to etching in the oxygen plasma than the planarizing polymer. The polysilanes are ideally suited for such procedures, since they are strongly absorbing in thin films permitting efficient light absorption, photosensitive over a broad spectral range, and resistant to  $\text{O}_2$  - RIE conditions due to the formation of a thin skin ( $50 - 100\text{\AA}$ ) of etch-resistant  $\text{SiO}_x$  on the polymer surface. Accordingly, we have utilized polysilanes in a bilayer configuration for the production and transfer of high resolution images generated by exposure in either the near UV ( $350\text{-}400\text{ nm}$ )<sup>20</sup> or in the mid UV ( $300\text{-}340\text{ nm}$ ) spectral regions.<sup>20</sup> The use of shorter wavelength exposure sources (e.g., KrF excimer lasers,  $248\text{ nm}$ ) in a 10X projection printing tool

leads to significantly improved resolution and allows the delineation of sub  $0.5\ \mu\text{m}$  features in a bilayer configuration (see Fig. 4).<sup>25</sup>

We have also demonstrated that submicron images can be produced in polysilanes by exposure to ionizing radiation such as e-beams and have studied the structure-sensitivity relationship for a number of representative derivatives.<sup>14</sup>

The bilayer processes described above used classical wet development steps for the production of images in the irradiated polysilane layer. However, high resolution images can also be produced directly in a thin polysilane layer by photoablative imaging. In this process, the polysilane is exposed to a high intensity radiation source (e.g., an excimer laser) during which the polymer spontaneously degrades and volatilizes. Since the image thus produced is subsequently transferred by gas phase  $\text{O}_2$  - RIE techniques, the procedure constitutes an all-dry, solventless lithographic process requiring no wet development step. The production and transfer of sub-micron images in such an all-dry process utilizing certain polysilane derivatives for imaging and an UV excimer laser exposure source have been successfully demonstrated.<sup>20</sup>

We have studied the photoablation process both by physical and chemical techniques. In the former, the polymer ablation was studied in situ using quartz crystal microbalance mass measurement procedures.<sup>20</sup> The ablation process seems to be primarily photo-thermal in nature and ablation thresholds of  $40\text{-}50\ \text{MJ}/\text{cm}^2\text{-pulse}$  were measured. The extent of physical ablation correlates with the energy density of the absorbed light. The products of ablation have also been studied by mass spectrometry<sup>26</sup> and the following conclusions drawn: (1) fragments containing small blocks of silicons are ejected. No evidence was obtained for the production significant quantities of monomeric silylenes (2) considerable carbon to silicon rearrangement occurs in the ablation process (3) cyclosilanes are not major products (4) substituent

side chains are stripped in a process probably involving the formation of chain silylsilylene intermediates and (5) similar gas phase products are produced both for UV and IR ablation suggesting a significant thermal component in the UV process.

The generation of images by projection printing in cases where the photomask features are of comparable size to the exposure wavelength is complicated by diffraction distortion of the mask features at the photoresist surface. Contrast enhanced lithography is a technique which employs a thin layer of an appropriate contrast enhancing layer coated on top of a conventional photoresist to improve the diffraction distorted mask image incident on the photoresist surface. Although a discussion of the concepts involved in the contrast enhancement of images is beyond the scope of this article, the reader is referred to the background information contained in the references.<sup>1</sup> However, consideration of the process suggests that a workable *contrast enhancing material* should possess a number of characteristics: (i) it should be thermally and oxidatively stable; (ii) the material should be very strongly absorbing at the exposure wavelength and bleach rapidly upon irradiation and (iii) it should be incompatible with the underlying photoresist so that the material boundaries are clearly delineated. Initially it was also felt that the contrast enhancing layer should be removable prior to the development of the exposed photoresist, but recent studies indicate that this characteristic is not essential.

Certain of the polysilane derivatives not only satisfy all of the above criteria but also absorb and bleach at shorter wavelengths than commercial materials thus providing the possibility of realizing the enhanced resolution intrinsic to short wavelength exposure sources.<sup>8,9,42,44</sup> A system composed of a conventional diazoquinone-Novolac type photoresist overcoated with a thin layer of poly(cyclohexylmethylsilane) has been studied in detail and significant improvements in

the image quality relative to the same photoresist without the contrast enhancing layer have been demonstrated.<sup>8,9,44</sup>

### Nonlinear Optical Properties

Finally, there is currently increased interest in the nonlinear optical properties of the materials due to their potential utility in optoelectronic or opto-optic devices for telecommunications and optical computing. In this regard, organic materials are of considerable interest because of their intrinsically large nonlinear susceptibilities, rapid response times and high threshold radiation damage values. Furthermore, the utilization of third order effects eliminates the stringent requirements for an acentric molecular environment thus expanding the range of useful materials to polymeric systems.

Studies of the third order susceptibilities ( $\chi^{(3)}$ ) of polymers to date have focused on highly polarizable materials containing conjugated  $\pi$  electron systems such as the polyacetylenes and diacetylenes, rigid rod aromatic polymers, ladder polymers, etc. While these materials have high intrinsic susceptibilities, many have other drawbacks such as limited processability, thermal and/or oxidative liability, nonideal spectral matching, etc.

The polysilanes represent a new class of potentially interesting nonlinear optical (NLO) materials. They are: (i) thermally and oxidatively stable, (ii) the  $\sigma$ -conjugated backbone is highly delocalized and absorbs very strongly in the UV region (iii) electronic substituent effects can be transmitted over large distances and (iv) the polarizability is large, anisotropic and dependent on backbone conformation. In fact, many of the electronic properties of the polysilanes more closely resemble conjugated  $\pi$  systems than saturated  $\sigma$  bonded carbon-based polymers. In addition, the polysilanes



are imposable to high resolution using standard lithographic techniques, a characteristic potentially useful for guided wave applications.

Initial NLO measurements on polysilane derivatives have revealed some interesting properties. Relatively large  $\chi^{(3)}$  values ranging from  $10^{-11}$  to  $10^{-12}$  esu<sup>27,28</sup> have been measured and the variation in these numbers with the film thickness suggests possible polymer orientational effects.<sup>28</sup> The resonant  $\chi^{(3)}$  value measured for thin films of poly(di-n-hexylsilane) ( $\sim 10^{-11}$  esu) is the largest reported for a polymeric system which is transparent in the visible and is comparable to values reported for rigid aromatic polymers such as poly(p-phenylenevinylene) and poly(p-phenylenebenzobisthiazole). Thermal effects on the third harmonic generation efficiency have been correlated with the known thermochromic characteristics of the polymers<sup>28</sup> and the picosecond time response<sup>29</sup> of the nonlinearity reported for poly(methylphenylsilane) is consistent with an electronic mechanism. In addition, biphotonic nonablative, nonlinear photochemical processes have been observed upon exposure to high intensity visible laser light. This photochemistry is anisotropic, and refractive index changes of greater than  $2.5 \times 10^{-2}$  (at 632.8 nm) have been induced due to selective polymer chain degradation in a direction parallel to the electric field of the laser light.<sup>30</sup> Birefringence changes of this magnitude are adequate for the fabrication of channel waveguides and birefringent grating structures.

Although the study of the NLO properties of polysilane derivatives is in its infancy, the unusual spectral properties, the substantial nonlinearities, the capacity for polymer orientation and the anisotropic photolability suggest that these materials are worthy of future investigation.

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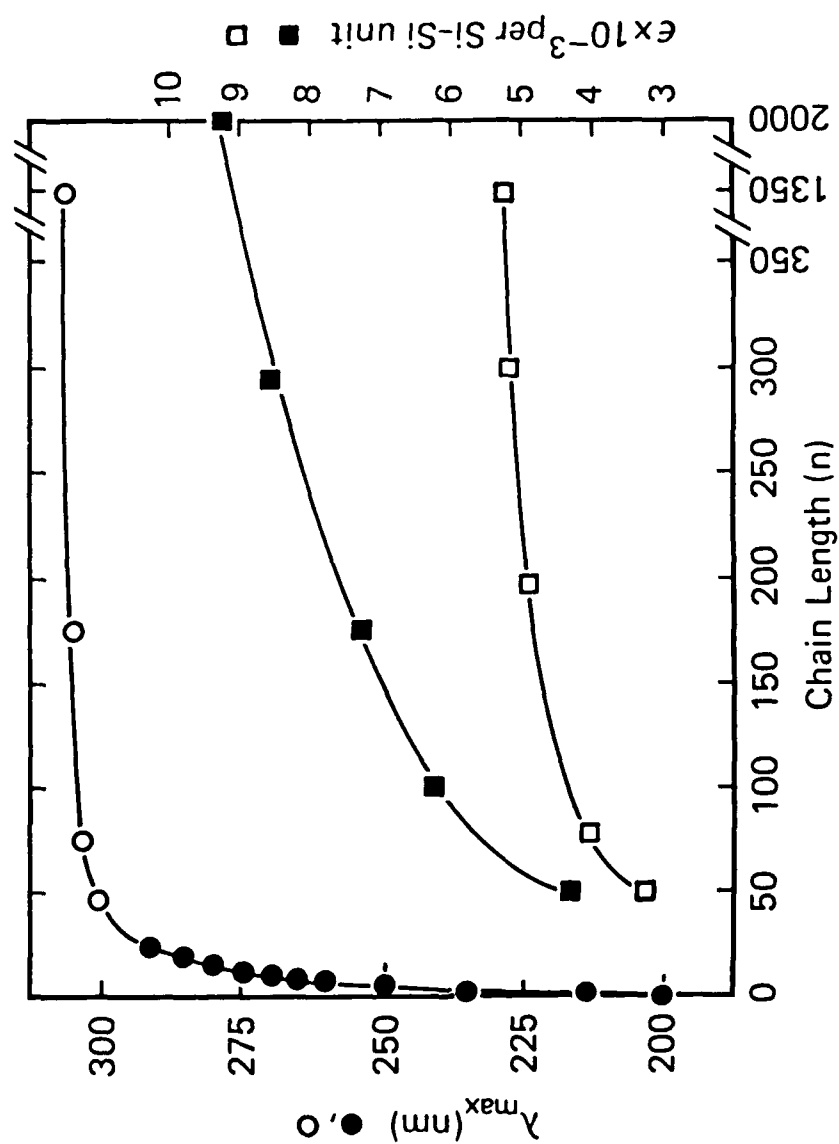
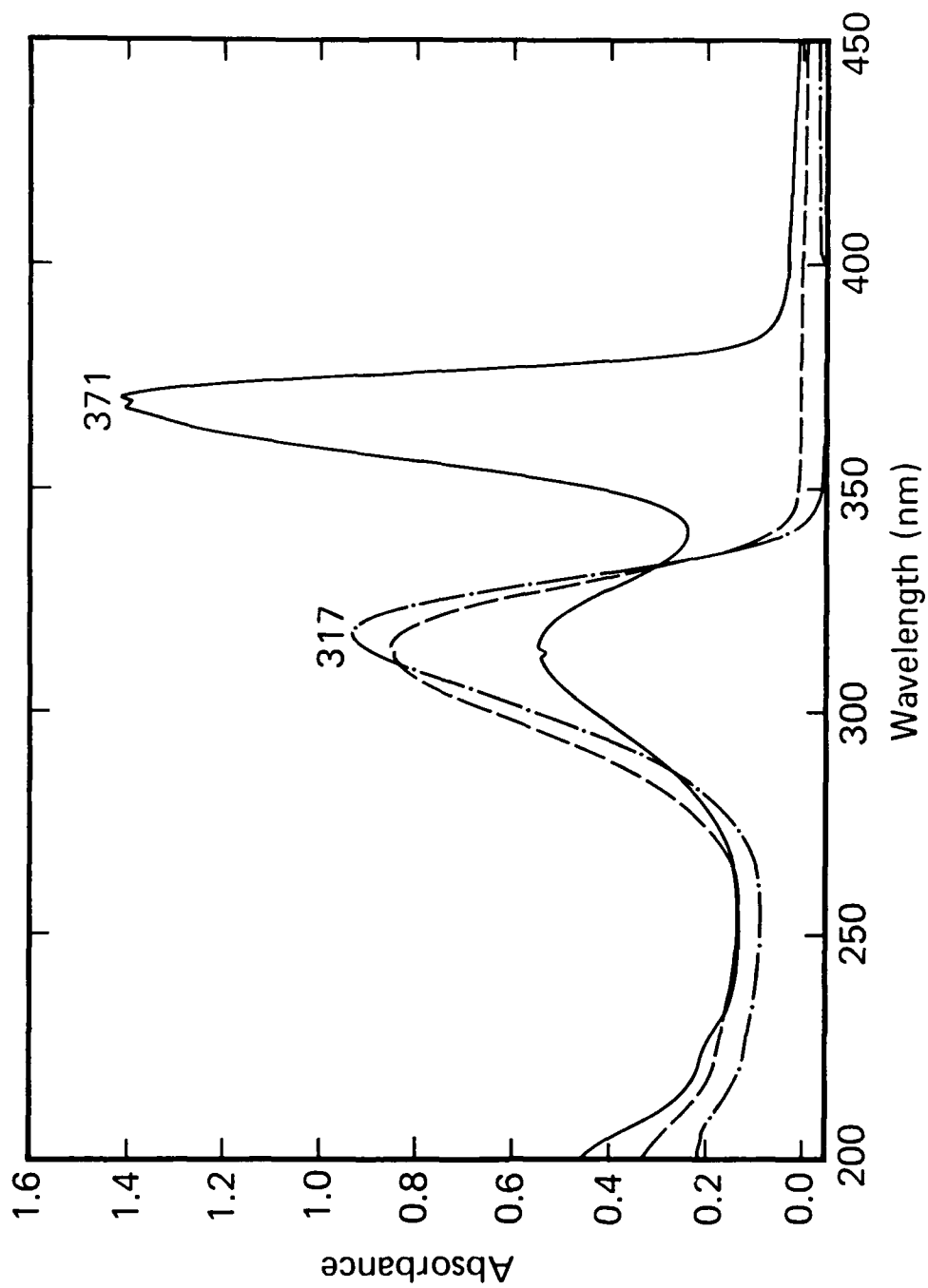
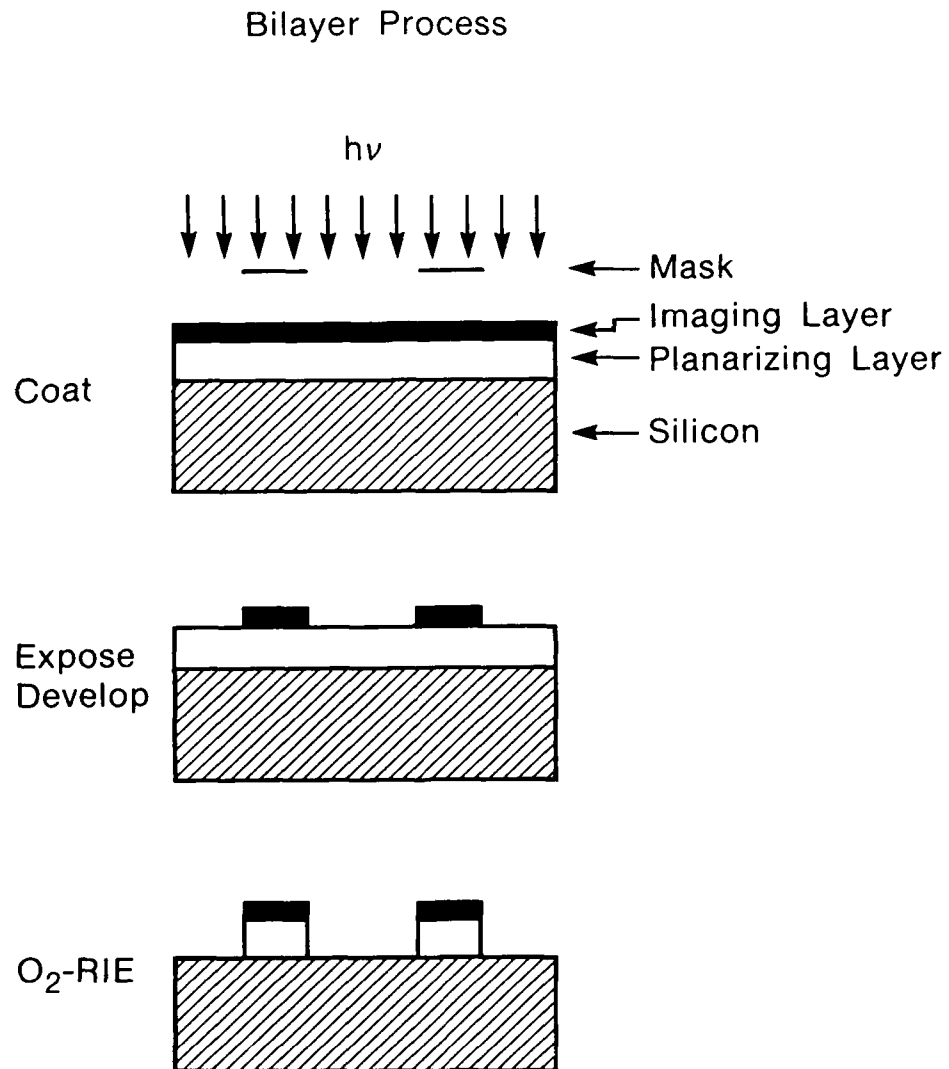


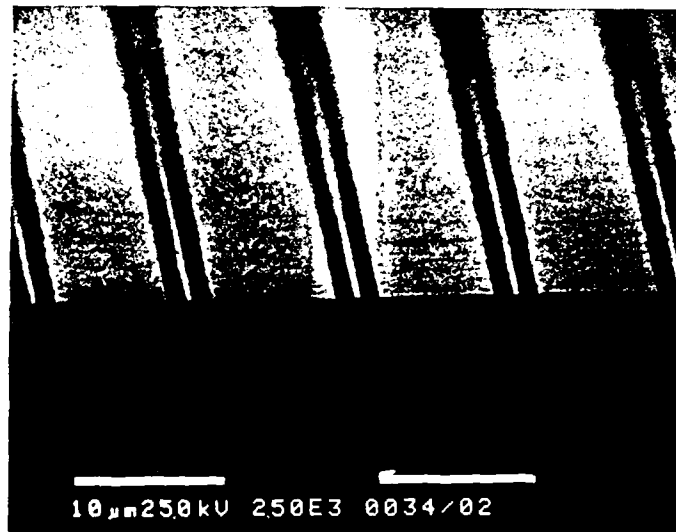
Figure 1. Absorption wavelength maxima ( $\lambda_{\max}$ ,  $\bullet$ ,  $\circ$ ) and extinction coefficients ( $\epsilon_{\text{sis}}$ ,  $\blacksquare$ ,  $\square$ ) as a function of oligomer/polymer chain length of n-units  $\{ \text{SiRR}' \}_n$ :  $\bullet$ ,  $\circ$  Me(Me<sub>2</sub>Si)<sub>n</sub>Me,  $\circ$  [(n-dodecyl)(MeSi)]<sub>n</sub>,  $\blacksquare$ ,  $\square$  [(n-dodecyl)(PhSi)]<sub>n</sub>.



**Figure 2.** UV absorption spectra of poly(di-n-hexysilane): (●-●) solution in hexane; (---) thin film run immediately after baking at 100°C; (-.-) thin film after standing at 20°C for 3 h.



**Figure 3.** Bilayer lithographic scheme utilizing a polysilane as the combination imaging and O<sub>2</sub>-RIE resistant barrier layer. For ablative self-development in an all-dry process, the image is produced and developed directly during the exposure step.



**Figure 4.** 0.75μm features generated in a bilayer of 0.2μm of poly (cyclohexylmethylsilane) coated over 2.0μm of a hardbaked photoresist using mid UV projection lithography.





Bilayer: 170nm poly(cyclohexylmethylsilane) over 1.0  $\mu\text{m}$  of hard baked AZ-type photoresist; 248 nm, 125 mJ/cm<sup>2</sup>, developed 80/20 butyl acetate-isopropanol, O<sub>2</sub>-RIE image transfer; (top) 0.4  $\mu\text{m}$ , (bottom) 0.5  $\mu\text{m}$



**Figure 5.** Images produced in a polysilane bilayer configuration using a deep UV, KrF excimer laser exposure source (248 nm).

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2. Miller, R.D., Sooriyakumaran, R., Fickes, G.N., Farmer, B.L., "Polymer Structural Studies of Unsymmetrically Substituted Dialkyl Polysilanes."
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